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(54) **Title:** NITRATE REMOVAL
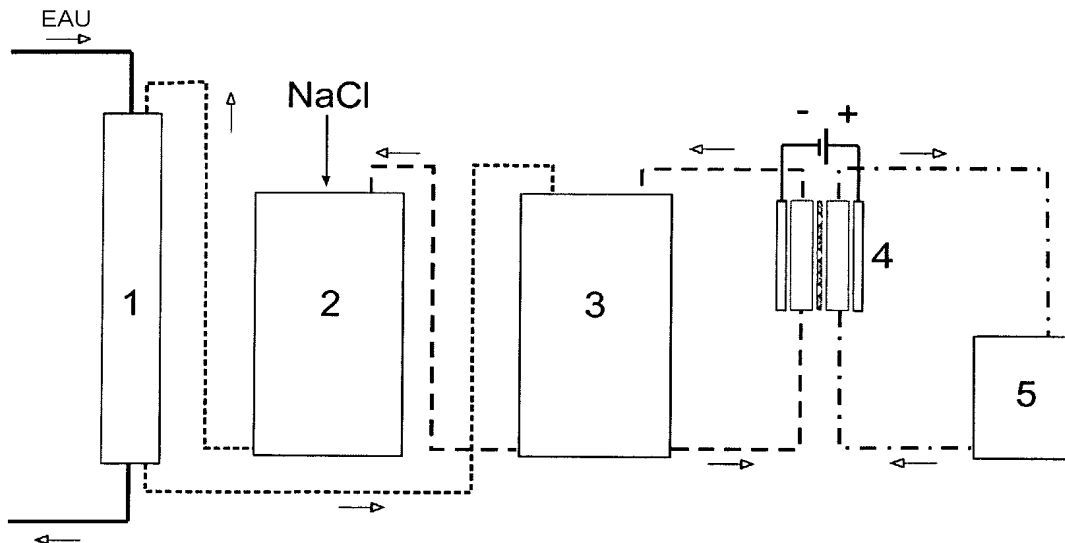
(57) **Abstract:** A process for removal and destruction of dissolved nitrate from water containing the same, which comprises a removal step in the form of a nitrate selective anion-exchange operation; a destruction step for nitrate destruction by electrochemical reduction thereof; a conditioning step, where solution resulting from the destruction step is adjusted to a chloride concentration suitable for use of said solution as a regenerant in teh anion-exchange operation; and a recycling step, where the solution resulting from the conditioning step is used as a regenerant in the anion-exchange operation.

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NITRATE REMOVAL

Technical Field of the Invention

The present invention relates to a process for removal and destruction of dissolved nitrate from water containing the same. More specifically, it relates to an
5   integrated process with nitrate selective ion exchange, electrochemical destruction of nitrate, and re-use of spent regenerant.

Background Art

10 During recent decades, nitrate contamination in raw water sources have been increasing due to the intensive use of nitrogenous fertilizers, changes in land-use patterns (from pasture to arable), and the contamination of sewage and industrial effluents. It has been found
15 that nitrate levels have been increasing in drinking water supplies in the European Economic Community, the United States, Canada, Africa, the Middle East, Australia, and New Zealand (Kappor and Viraraghavan, 1997). Because an increased nitrate uptake can link to
20 several health hazards causing methaemolobinaemia or cancer risks due to nitrosamines or nitrosamides, limits have been set up to regulate the maximum nitrate levels in drinking water. In Europe, an EEC Directive on the quality of drinking water for human consumption specifies
25 a maximum admissible concentration of 50 mg NO_3^-/l, but a guide level of 25 mg NO_3^-/l is recommended (European Community, 1980). The U.S. EPA establishes a maximum contaminant level (MCL) of 10 mg NO_3^--N/l corresponding to 44 mg NO_3^-/l (Pontius, 1993). The Health and Welfare
30 Canada has established a maximum acceptable concentration (MAC) of 10 mg NO_3^--N/l and the nitrite of 3.2 mg/l when nitrates and nitrites are measured separately in drinking water (Health and Welfare Canada, 1993).

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Several technologies can be used for nitrate removal from waters. The chemical technologies include ion exchange and catalytic denitrification. The membrane technologies involve reverse osmosis, nanofiltration, electrodialysis and electrodeionization. Biological denitrification has also been applied. When comparing the various technologies in terms of effectiveness, ease of operation, reliability, cost and suitability for environmental regulation, ion exchange is found to be a highly competitive technology and is used in commercial large-scale applications, especially for drinking water treatment.

Conventional ion-exchange technology involves a process, in which the nitrate contained in water is exchanged with another anion that is already adsorbed on the strong basic ion-exchange resin. Also competing anions present in the water take part in this exchange and are adsorbed to the resin. This condition lowers the efficiency of nitrate removal from waters contaminated with e.g. sulphate.

After a period of operation, the exchange capacity of the resin is exhausted. The exhausted resin is then regenerated with a regeneration chemical. During the regeneration cycle, the nitrate is released from the resin and a waste stream is produced together with the regeneration chemical. The nitrate can be reduced to nitrogen, but the waste stream containing the regeneration chemical is still remaining. Disposal of the waste stream may lead to a significant waste disposal cost or regulatory complications as well as to loss of the regeneration chemical. The disposal of the waste solution is a big challenge for the application of the ion exchange technology. Attempts to recycle the regenerating solution have been made, but have failed because competitive anions are accumulated in the spent regenerant and the regeneration efficiency is not maintained.

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The European patent application 291,330 discloses a process for treatment of ground-water containing nitrate, comprising the steps of contacting the water with an ion-exchange resin, regenerating the exhausted ion-exchange resin with a regenerant, and reconstituting the spent regenerant by subjecting it to electrolysis. In this process, however, chlorine gas may undesirably be evolved. In addition, sodium hypochlorite, which will destroy the ion-exchange resin, will be formed.

The British patent 1,432,020 discloses a process for recovery of spent regenerating solutions for re-use in an ion-exchange system. This is an extensive process aiming at recovering the different components of the spent regenerating solutions by precipitation and electrodialysis.

Summary of the Invention

One object of the present invention is to provide an integrated process allowing efficient removal and destruction of nitrate from waters contaminated with other anions.

A second object of the present invention is to provide such a process where spent regenerant solution can be continuously re-used.

Another object of the present invention is to provide such a process which does not give rise to any waste streams.

Still another object of the present invention is to provide such a process where competing anions are not accumulated in the re-used regenerant.

A further object of the present invention is to provide such a process where the regeneration efficiency is maintained.

Other objects of the invention should be apparent to a person skilled in the art when reading the more detailed description of the invention as presented below.

4

These objects are achieved by a process for removal and destruction of dissolved nitrate from water containing the same, which comprises

- a removal step in the form of an anion-exchange operation, where nitrate is eliminated from said water in the form of a more concentrated solution thereof, said anion-exchange operation being nitrate selective;

- a destruction step, where said more concentrated nitrate solution is subjected to an electrolysis operation for nitrate destruction by electrochemical reduction thereof;

- a conditioning step, where solution resulting from the destruction step is adjusted by the addition of chloride ions so as to enable use of said solution as a regenerant in the anion-exchange operation while maintaining an operating capacity of said anion-exchange operation which is substantially unchanged from one anion-exchange operation to another; and

- a recycling step, where solution resulting from the conditioning step is used as a regenerant in the anion-exchange operation.

The use of a removal step with a nitrate selective ion-exchange operation makes it possible to remove nitrate ions also from waters contaminated with competing anions, without substantially lowering the efficiency of the removal.

The destruction step with an electrolysis operation where nitrate is reduced to nitrogen assures effective destruction of nitrate.

The conditioning step makes it possible to maintain the regenerating efficiency of the recycled regenerant by a sufficiently high chloride concentration to displace nitrate ions from the ion-exchange resin and thereby to maintain the operating capacity of the ion-exchange operation.

5

The fact that a minimum of competing anions are adsorbed to the ion-exchange resin, combined with efficient regeneration of the resin, means that less competing anions are accumulated in the spent regenerant.

The recycling step completes the process and enables an integrated process with complete re-use of spent regenerant and no waste streams.

For the sustainable operation of an ion-exchange system with continuous recycling of spent regenerant, three aspects must simultaneously be considered:
- the nitrate contained in the spent regenerant must be destructed as much as possible
- the accumulation of competitive anions in the spent regenerant must be discontinued in some way, and
- high regeneration efficiency for the ion-exchange bed must be maintained as the concentration of regeneration solution is changed with continued regeneration cycles.

Brief Description of the Drawings

Figure 1 shows a flow diagram for a typical system configuration to perform the process of the present invention.

Figure 2 and 3 show results from Example 2 below.

Detailed Description of Preferred Embodiments of the Invention

The integrated process comprises four steps: nitrate selective removal from water by ion exchange, electrochemical destruction of the nitrate in spent regenerant, conditioning of the spent regenerant, and recycling of the conditioned regenerant. According to the invention, preferably all, but at least a major part, of the spent regenerant is recycled.

The key points of the process are to keep mass balances for accumulated anions in a succession of repeated process cycles, and to maintain the regenerating

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and operating efficiencies throughout repeated cycles.
When sulphate is present the mass balance for sulphate is
achieved by a steady-state accumulation in spent
regenerant.

5   The steady state is a dynamic phenomenon related to
the re-use of spent regenerant in multiple operation and
regeneration cycles. It depends on the properties of the
ion-exchange resin, the concentration of anions in the
raw water, and the conditions of operation and

10   regeneration. If nitrate removal can be performed under
such steady state conditions, a continuous process can be
set up for multiple operating and regenerating cycles
without the discharge of spent regenerant.

       The efficiencies of operation and regeneration are

15   maintained in two ways. In regeneration, the nitrate
adsorbed in an operation cycle must be replaced by the
regenerant as much as possible. Although both chloride
and sulphate may theoretically be used as regenerants for
an anion resin to displace nitrate, high concentration of

20   sulphate in a regeneration solution gives a negative
influence on regeneration efficiency. In operation, the
removal of nitrate is achieved mainly by selective
displacement using nitrate selective anion-exchange
resins.

25

Selective nitrate removal by ion-exchange
       In the first step of the process, nitrate is removed
from water by a selective anion-exchange resin. A nitrate
selective resin has higher affinity for nitrate than for

30   other major anions present in the water. The purposes of
using a nitrate selective resin are to increase the
operating capacity of the ion-exchange operation when the
ratio of competing anions, e.g. sulphate, to nitrate is
high in the water; to reduce the adsorption of other

35   anions to the ion-exchange resin; and to decrease the
accumulation of other anions in the regeneration
solution.

7

Two commercial nitrate selective anion-exchange resins (IMAC HP555 from Rohm & Haas and A520E from Purolite) have been tested in their chloride forms for ion-exchange. The relative affinities of these types of
5   resins for anions present in water are:

$$NO_3^- > SO_4^{2-} > Cl^- > HCO_3^- \tag{1}$$
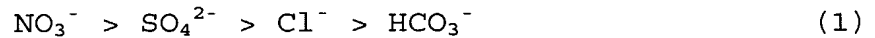
The relative affinities of a regular strong base anion-exchange resin for these anions are usually as follows:
10

$$SO_4^{2-} > NO_3^- > Cl^- > HCO_3^- \tag{2}$$
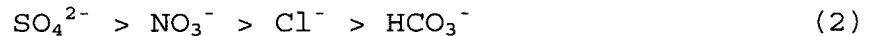
Because the selective resins have a higher affinity for nitrate compared to other major anions present in nature waters, the adsorption of other anions becomes much less
15   than to regular anion-exchange resins. The higher affinity of a resin for nitrate, the larger nitrate removal capacity the resin has.

When the nitrate removal capacity of the resin bed is exhausted in an operation cycle, the anions adsorbed
20   together with nitrate in the operation cycle are replaced by chloride. During a regeneration cycle, co-current regeneration is carried out to recover the capacity.

Although it is impossible to totally separate nitrate from other anions in the ion-exchange operation
25   cycle, the selective displacement using the nitrate selective resin makes the adsorption of other anions limited.
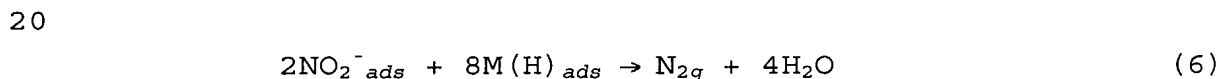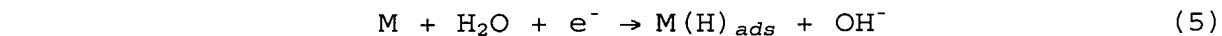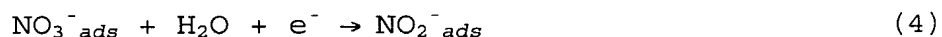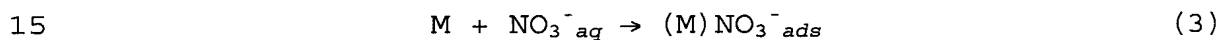
Carbonate, chloride and sulphate are major anions in most of nature waters. As a nitrate selective resin is
30   used for the ion-exchange system and sodium chloride is used as the regenerant, sulphate is mainly concerned for the anion accumulation in spent regenerant according to the relative affinities of the resin for these anions (equation 1).

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Electrochemical destruction of nitrate

The nitrate reduction can be performed by any electrochemical method suitable for that purpose, but is preferably carried out in a two-compartment
5   electrochemical cell equipped with cation-exchange membranes. A wide range of commercially available cation exchange membranes are suitable to incorporate in the cell and be used in the process. As cathode, graphite, platinum, platinised titanium, lead, nickel, nickel mesh,
10   copper, or copper mesh electrodes have proved to be especially efficient.

The nitrate reduction on the cathode can be described as follows:

15
$$M + NO_3^-{}_{aq} \rightarrow (M)NO_3^-{}_{ads} \tag{3}$$

$$NO_3^-{}_{ads} + H_2O + e^- \rightarrow NO_2^-{}_{ads} \tag{4}$$

$$M + H_2O + e^- \rightarrow M(H)_{ads} + OH^- \tag{5}$$
20
$$2NO_2^-{}_{ads} + 8M(H)_{ads} \rightarrow N_{2g} + 4H_2O \tag{6}$$

Catalytic hydrogenation could be a part of the reduction of the nitrite and/or nitrate adsorbed on
25   nickel graphite or platinum cathodes. On lead and copper cathodes electronation/protonation are the main reactions of the nitrate reduction

$$NO_3^-{}_{aq} \rightarrow NO_2^-{}_{aq} \tag{7}$$
30
$$2NO_2^-{}_{aq} + 8H^+ + 2e^- \rightarrow N_2 + H_2O \tag{8}$$
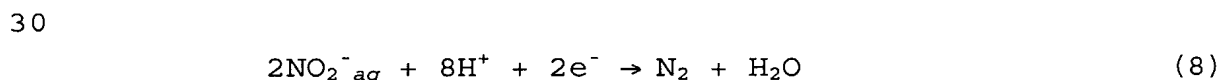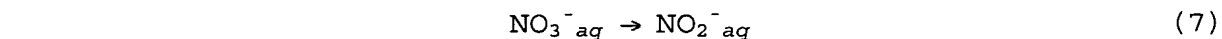
The main side reactions are hydrogen evolution

35
$$H_2O + 2e^- \rightarrow H_2 + OH^- \tag{9}$$
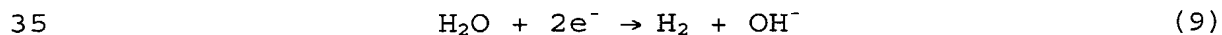
and nitrite reduction to ammonia

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$$NO_2^-{}_{aq} + 8H^+ + 6e^- \rightarrow NH_3 \qquad (10)$$

The anolyte contains sulphuric acid. In the anodic
compartment the main reaction is water electrolysis,
oxygen evolution and proton generation:

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad (11)$$
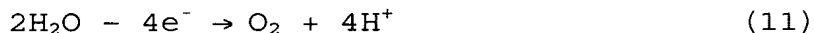
Protons generated during the water oxidation are
transferred to the cathodic compartment.

The main roles of the cation exchange membrane are
to prevent re-oxidation of the intermediates and the
products of the nitrate reduction process, to transfer
protons generated on the anode from the anodic
compartment to the cathodic compartment, and to avoid
chlorine evolution on the anode, which would lead to the
presence of active chlorine or to the production of
hypochlorite (ClO^-) or chlorate (ClO_3^-). These oxidative
species can cause serious damage to the anion exchange
resin.

Conditioning of spent regenerant

In addition to discontinued accumulation of
competing anions in spent regenerant, a high regeneration
efficiency at such steady-state concentrations is
required in order to have a low residual nitrate in
treated water during succesive operation cycles. A high
regeneration efficiency is maintained as for instance the
sulphate concentration in the spent regenerant increases
during the re-using cycles until a steady state is
reached. It has been found that the regeneration
efficiency is decreased as the sulphate concentration is
relatively higher and the chloride concentration is
relatively lower. However, the negative influence of
sulphate on the regeneration can be reduced when a
relatively higher concentration of chloride and/or a

relatively higher ratio of chloride to sulphate is kept
in the spent regeneration solution. A NaCl concentration
higher than about 9 %wt (corresponding to a chloride
concentration higher than about 5 %wt) and/or a ratio in
equivalents of chloride to sulphate higher than about 6
in the spent regeneration solution is an especially
preferred value to keep a high efficiency of
regeneration.

     Moreover, a suitable regeneration level should also
be considered. The regeneration level is defined as the
weight of regenerant used to regenerate a certain volume
of ion-exchange resin. The absolute regeneration level
includes regenerant added in the conditioning step and
regenerant re-used from the last cycle. The absolute
regeneration level does not strongly affect the economy
of the process because the actual regeneration level
(only accounting for regenerant added in conditioning) is
much lower than the absolute regeneration level. However,
the regeneration level affects the operating capacity and
the quality of treated water in the following cycle. An
absolute regeneration level higher than about 350 g
NaCl/l resin is recommended to keep a high efficiency of
regeneration.

     In addition, deionized or softened water should be
used for conditioning of the regenerant and rinsing of
regenerated resin to prevent from the precipitation of
calcium sulphate and/or magnesium sulphate.

Recycling of conditioned regenerant

     After nitrate destruction and conditioning, the
spent regenerant is re-used for regeneration of the an-
ion exchange operation during another process cycle.
Thus, a process which does not give rise to any waste
streams is provided.

     Figure 1 schematically shows one embodiment of an
apparatus for performing the process according to the

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invention. The apparatus shown in the figure includes the
following elements: an ion-exchange column 1, a
regenerant tank 2, a spent regenerant tank 3, an
electrochemical cell 4, and an anolyte tank 5.

5   Said apparatus works in the following way: Nitrate
contaminated water passes through the ion-exchange column
1, loaded with chloride ions, where nitrate ions present
in said water are adsorbed on the nitrate selective
anion-exchange resin and are replaced by chloride ions.

10 When the ion-exchange column 1 is exhausted, it is
regenerated with a sodium chloride solution from the
regenerant tank 2. Nitrate is removed and replaced by
chloride ions.

The spent regenerant solution, containing nitrate,

15 is collected in the spent regenerant tank 3. Spent
regenerant from the spent regenerant tank 3 and anolyte
from the anolyte tank 5 are circulated through the
electrochemical cell 4, where nitrate is reduced to
nitrogen gas.

20   The spent regenerant is then transferred to the
regenerant tank 2, where it is conditioned by addition of
sodium chloride.

The conditioned regenerant in the regenerant tank 2
is re-used for regeneration of the ion-exchange column 1

25 in another process cycle.

In another embodiment, the apparatus comprises
multiple ion-exchange columns to allow use of one column
for nitrate removal when another is being regenerated.

30 Examples

A nitrate removal process is demonstrated in the
following examples. The process is an integrated process
with nitrate removal by nitrate selective ion-exchange,
destruction of nitrate in the spent regenerant in an

35 electrochemical cell, and the full re-use of the
regenerant by hindering the accumulation of sulphate and

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conditioning the concentration of sodium chloride in the spent regeneration solution.

A synthetic waste water containing 100 mg/l of nitrate, 500 mg/l of sulphate and 160 mg/l of chloride was used as raw water. The concentration of the synthetic water represented a relatively harsh situation compared to natural waters, especially on the ratio of nitrate to sulphate. During operation, the synthetic water was treated by passing it through an ion-exchange column (Ø 29 mm) with 20 g of nitrate selective resin (IMAC HP555 or A520E). The operation flow rate was usually 20-25 bed volumes/h (BV/h).

The nitrate concentration in the effluent was controlled to be less than 40 mg NO_3^-/l, which was taken as the end point of an operation cycle. As the nitrate concentration in effluent reached 40 mg NO_3^-/l, the operation cycle was stopped, a regenerating cycle was then started using NaCl solution. Meanwhile, the spent regenerant was collected for electrolysis, conditioning and re-use in the next regeneration cycle.

All experiments were carried out with commercially available ElectroMP and ElectroSyn cells equipped with Nafion 324 or Nafion 350 type cation exchange membranes. A wide range of commercially available cation exchange membranes are suitable to incorporate in the cell and be used in the process. The ElectroMP cell has a minimum geometrical surface area of 100 cm^2. The minimum surface area in the EletroSyn cell is 400 cm^2 for each electrode. PVDF or PP frames and EPDM gaskets (O-rings) were incorporated in the cell for proper sealing. A PE turbulence promoter provided uniform fluid distribution and good mass transfer conditions. The operation mode for all experiments was batch mode.

As cathode, a graphite electrode was used in such a way that solid graphite acted as current feeder which was pressed/glued to graphite felt. The catholyte compartment therefore was packed; the distance between the membrane

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and the cathode was reduced to 2 mm from the original
9 mm gap.

The electrolytes of the anodic and cathodic chambers
had a volume of 2 litres in the ElectroMP cell. The
5   anolyte was 0.9 M of sulphuric acid. The acid
concentration remained stable after several cycles of
electrolysis. The anolyte level was maintained the same;
deionized water was added to the anolyte, as a part of
the water had been electrolysed.

10   The pressure on the cell was maintained at 0.2 bar,
which provided a constant flow in each compartment. The
temperature of the electrolytes was below 40 °C. The
process parameters are summarised in Table 1.

15   Table 1
The process parameters of the electrochemical nitrate
reduction

Active electrode surface	200-400 cm^2
Current density	1 kA/m^2
Electrode gap	2 mm cathode side;
	9 mm anode side
Temperature	25-34 °C
Superficial velocity	0.5 m/s
Membrane	Nafion® 324, 350

20   The operation-regeneration-operation cycles were
continuously run without discharge of spent regenerant. A
steady-state concentration of sulphate was reached in the
spent regeneration solution after the initial cycles.
Because of the complete re-use of spent regenerant, a
25   high regeneration level and co-current regeneration were
used for this process.

The efficiency of the continuous process for nitrate
removal in such a succession of repeated cycles is
illustrated in the following examples.

30

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Example 1

    The effluent quality of the ion-exchange system was good in continuous operation cycles. As shown in Table 2 and Table 3, the average concentrations of residual
5   nitrate in the effluent were below 15 mg NO_3^-/l when the control limit was set to less than 40 mg NO_3^-/l. The concentrations of other anions in the effluent were close to those in the raw water. Nitrate was selectively removed in the operation cycles.
10   A comparison between an early cycle and a later cycle is also given in Table 2 and Table 3. Although the early operation cycle (cycle 2) was regenerated by a regenerant containing a relatively lower concentration of sulphate and the later operation cycle (cycle 9) was
15 regenerated under a high (steady-state) concentration of sulphate, the effluent quality did not show any significant difference between these operation cycles. The efficiency of nitrate removal in operation was maintained throughout the operation cycles.
20

Table 2

The effluent quality of the ion-exchange column using the
nitrate selective resin IMAC HP555

Cycle 2					Cycle 9				
Effluent (BV)	NO$_3^-$ (mg/l)	SO$_4^{2-}$ (mg/l)	Cl$^-$ (mg/l)	pH	Effluent (BV)	NO$_3^-$ (mg/l)	SO$_4^{2-}$ (mg/l)	Cl$^-$ (mg/l)	pH
12	10	4	584	6.27	11	6	0	537	6.73
30	8	26	563	6.19	29	7	16.2	558	6.74
48	11	158	470	6.51	48	7	474	129	6.75
66	6	377	311	6.19	67	7	358	307	6.24
84	6	501	213	6.14	86	6	441	192	6.42
104	5	547	181	6.21	104	7	526	184	6.34
122	6	557	171	6.21	125	7	538	177	6.40
142	7	555	175	6.25	144	8	567	183	6.41
163	11	557	173	6.32	163	10	536	172	6.48
172	14	558	174	6.27	173	11	534	173	7.19
181	17	551	172	6.24	182	14	561	179	6.44
190	21	545	174	6.18	191	18	567	180	6.38
199	28	542	170	6.23	200	19	534	169	6.35
209	34	538	170	6.18	209	25	527	167	6.36
218	39	537	174	6.19	218	31	529	167	6.37
Average	15	437	258	6.24	Average	12	447	232	6.51

Notes: Cycle 2 is an early operation cycle that has been regenerated
by re-use of spent regenerant containing a relatively lower
concentration of sulphate. Cycle 9 is a later operation cycle that
has been regenerated using spent regenerant containing the steady-
state concentration of sulphate.

Table 3

The effluent quality of the ion-exchange column using the nitrate selective resin A520E

Cycle 2					Cycle 9				
Effluent (BV)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Cl^- (mg/l)	pH	Effluent (BV)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Cl^- (mg/l)	pH
11	9	0	537	6.80	10	10	6	549	6.81
28	9	12	566	6.49	28	10	14	565	6.54
45	8	89	513	6.36	46	10	118	488	6.22
63	8	325	338	6.02	64	15	609	598	6.12
80	8	470	221	6.12	81	8	477	230	6.00
98	7	521	189	5.98	98	7	534	192	6.06
117	7	530	174	5.71	115	7	554	185	5.66
134	7	529	172	6.07	132	7	554	180	5.57
152	10	538	178	5.54	150	8	561	180	5.55
162	8	539	175	5.60	158	8	550	178	5.54
170	9	533	177	5.61	168	10	564	179	5.57
180	10	538	175	5.61	177	11	550	173	5.56
188	12	531	174	5.55	186	8	552	177	5.66
197	14	529	174	5.58	195	10	557	178	5.67
206	17	532	173	5.70	203	13	545	175	5.50
214	20	530	171	5.78	212	18	554	177	5.53
223	26	567	181	5.79	221	22	547	175	5.50
232	28	523	168	5.90	230	25	545	172	5.81
240	34	503	163	5.61	238	31	539	172	5.58
249	40	519	165	5.68	247	46	533	168	5.66
Average	14	443	239	5.88	Average	14	473	255	5.81

5

Notes: Cycle 2 is an early operation cycle that has been regenerated by re-use of spent regenerant containing a relatively lower concentration of sulphate. Cycle 9 is a later operation cycle that has been regenerated using spent regenerant containing a steady-
10   state concentration of sulphate.

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Example 2

Spent regenerant was continuously re-used in a
regeneration-operation-regeneration chain of repeated
cycles. Two nitrate selective resins, IMAC HP555 (Rohm &
5   Haas) and A520E (Purolite), were tested for their
regeneration and operation efficiencies, and for the
accumulation of sulphate in spent regenerant. As shown in
Figure 2, the accumulation of sulphate in the spent
regeneration solutions was terminated after certain
10   regeneration-operation-regeneration cycles. The
concentration of sulphate in the spent regeneration
solutions reached a steady state without discharge of
spent regenerant. This means that a nitrate removal
process can be performed with a succession of repeated
15   cycles as the regeneration efficiency can be maintained
under steady-state conditions. Figure 3 shows that the
operation capacities of the ion-exchange columns were
very stable during the regeneration-operation-
regeneration cycles, also when the sulphate accumulation
20   in spent regenerant had reached steady state. More
detailed information on the regeneration parameters and
operation features is given in Table 4 (for IMAC HP555)
and Table 5 (for Purolite A520E). The results indicate
that the quality of the effluents was not changed during
25   the repeated process cycles.

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Table 4

The results of the column tests using the nitrate
selective resin IMAC HP555

Cycle	Regeneration		Operation			
			(average in effluent)			
	NaCl	Level	NO_3^-	SO_4^{2-}	Cl^-	pH
	(%)	(g NaCl/l resin)	(mg/l)	(mg/l)	(mg/l)	
1	6.4	459	16	400	144	6.88
2	8.9	482	12	415	276	6.24
3	7.4	476	13	412	282	6.56
4	9.0	486	13	383	287	6.50
5	9.0	486	9	422	253	6.49
6	9.0	486	13	427	250	6.57
7	9.0	486	13	425	245	6.48
8	9.0	486	11	432	248	6.52
9	9.0	486	14	452	228	6.57

5

Table 5

The results of the column tests using the nitrate
selective resin A520E

Cycle	Regeneration		Operation			
			(average in effluent)			
	NaCl	Level	NO_3^-	SO_4^{2-}	Cl^-	pH
	(%)	(g NaCl/l resin)	(mg/l)	(mg/l)	(mg/l)	
1	8.9	458	16	447	248	5.78
2	9.0	462	14	443	239	5.96
3	9.0	462	14	439	238	6.05
4	9.0	462	12	441	244	5.95
5	9.0	462	12	448	248	6.06
6	9.0	462	13	459	239	5.99
7	9.0	462	11	430	230	6.03
8	9.0	462	11	470	240	5.85
9	9.0	462	14	473	255	5.86
10	9.0	462	15	440	253	5.88
11	9.0	462	16	432	232	6.11

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Example 3

The nitrate contained in spent regeneration solution
was destructed by an electrochemical reduction process
5   before conditioning. The catholyte was composed of sodium
chloride, sodium nitrate and sodium sulphate. The initial
ratios of the three main components of the catholyte were
varied since the concentration of the anions changes
after several cycles of regeneration of the nitrate
10   selective anion exchange resin. The sulphate
concentration was varied between 32 and 134 mmol/l.
Selective nitrate reduction and water electrolysis were
the two main reactions. The conditions of the
electrolysis were set to reduce the nitrate selectively.
15   Over 99 % of the nitrate in the catholyte was reduced.

Sulphuric acid (0.8-0.9 M) was used as anolyte and
water electrolysis with oxygen evolution was the main
reaction in the anodic compartment. The protons generated
from the electroysis were transferred into the cathodic
20   compartment.

The pH of the catholyte and the anolyte remained
stable after several cycles of nitrate removal and
reduction. Volumetric changes in the two compartments
resulted in an increased level in the catholyte and a
25   decreased in the anolyte. The anolyte level was adjusted
by water addition after each cycle of the reduction.

In the anodic compartment the electrolyte was not
changed. In a total of over the 150 hours of operation
there was no need for acid addition to the sulphuric acid
30   anolyte. In the cathodic compartment the same sodium
chloride solution was used.

The parameters and results are shown in Table 6-9.

20

Table 6

Results obtained from the electrochemical reduction of
nitrate in an effluent in which the initial sulphate
concentration was lower than the nitrate concentration.
The conversion rate for nitrate was over 91 % and the
current efficiency was 46 %.

			Catholyte				Anolyte	
Time	Current	Tension	Volume	SO_4^{2-}	NO_3^-	NO_3^-	Volume	H^+
(h)	(A)	(V)	(l)	(mmol/l)	(mmol/l)	(mg/l)	(l)	(mol/l)
0	20	4.40	2.00	32.03	86.44	5360	2.00	0.80
1.0	20	4.35	2.00	31.89	68.11	4223	1.95	
2.0	20	4.40	2.10	31.84	31.76	1969	1.85	
3.0	20	4.50	2.10	31.41	7.70	478	1.80	
4.0	20	4.60	2.20	30.66	1.43	88	1.75	0.91

Table 7

Results obtained from the electrochemical reduction of
nitrate in an effluent in which the initial sulphate and
nitrate concentrations were in the same range. The
conversion rate for nitrate was over 92 % and the current
efficiency was 84 %.

			Catholyte				Anolyte	
Time	Current	Tension	Volume	SO_4^{2-}	NO_3^-	NO_3^-	Volume	H^+
(h)	(A)	(V)	(l)	(mmol/l)	(mmol/l)	(mg/l)	(l)	(mol/l)
0.0	20	4.20	2.20	50.2	53.1	3296	2.00	0.80
1.0	20	4.00	2.20	49.1	5.2	310	1.95	
2.0	20	4.00	2.20	49.2	0.2	10	1.85	
2.5		4.00	2.20	48.8	0.1	7		
3.0	20	4.10	2.25	47.9	0.3	19	1.85	
3.5		4.20	2.25	48.1	0.0	0	1.80	
4.0	20	4.20	2.30	48.0	0.0	0	1.78	0.90

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Table 8

Results obtained from the electrochemical reduction of
nitrate in an effluent in which the initial sulphate
concentration was higher than the nitrate concentration.
The conversion rate for nitrate was over 80 % and the
current efficiency was over 61 %.

Time	Current	Tension	Catholyte				Anolyte	
			Volume	SO_4^{2-}	NO_3^-	NO_3^-	Volume	H^+
(h)	(A)	(V)	(l)	(mmol/l)	(mmol/l)	(mg/l)	(l)	(mol/l)
0.0	20	4.34	2.20	80.5	42.4	2627	2.00	0.79
1.0	20	4.40	2.20	76.1	9.1	567	1.95	
2.0	20	4.50	2.30	75.4	0.5	32	1.85	0.83
0.0	20	4.40	2.20	96.5	42.0	2601	1.95	0.80
1.0	20	4.40	2.20	94.0	11.2	696	1.90	
2.0	20	4.60	2.30	93.5	0.9	53	1.85	0.84

Table 9

Results obtained from the electrochemical reduction of
nitrate in an effluent in which the initial sulphate
concentration was close to the highest concentration that
could be obtained with the nitrate selective ion exchange
resin after several cycles of regeneration. The
conversion rate for nitrate was close to 90% and the
current efficiency was over 52 %.

Time	Current	Tension	Catholyte				Anolyte	
			Volume	SO_4^{2-}	NO_3^-	NO_3^-	Volume	H^+
(h)	(A)	(V)	(l)	(mmol/l)	(mmol/l)	(mg/l)	(l)	(mol/l)
0.0	20	4.30	2.00	134.4	31.0	1924	2.00	0.82
1.0	20		2.00	129.5	3.3	206	1.95	
2.0	20		2.10	129.4	0.1	8	1.85	
3.0	20		2.10	129.3	0.1	6	1.80	
4.0	20	4.57	2.20	129.0	0.0	<5	1.75	0.88

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As shown by the results, the nitrate reduction was successfully carried out in an electrolyte containing sulphate and chloride in high concentrations. The current efficiency of the nitrate reduction depends on the

5   initial nitrate concentration and on the conversion rate. The reduction process is more efficient in solutions which are more concentrated on nitrate. The selectivity of the nitrate reduction was not effected by the increasing sulphate concentration. Increasing initial

10 nitrate/sulphate ratio resulted in an increase in the nitrate reduction efficiency as indicated in Table 10.

Table 10
The current efficiency of the nitrate reduction depends

15 on the ratio of nitrate to sulphate

Ratio of NO_3^-/SO_4^{2-}	Current efficiency (%)
> 1	~ 46
< 1	> 52

Example 4
        As shown in Table 11, the ratio of chloride to

20 sulphate in the regeneration solution played an important role for the regeneration efficiency. A high ratio of chloride to sulphate should be kept in a spent regeneration solution in order to maintain a good regeneration efficiency and to decrease residual nitrate

25 in effluent in the following operation cycles.

Table 11

Comparison of the regeneration efficiencies for IMAC
HP555 with different ratios of chloride to sulphate in
the regenerant

Regeneration			Capacity	Operation			
NaCl	SO_4^{2-}	Ratio		NO_3^-	SO_4^{2-}	Cl^-	pH
				in effluent			
(meq/l)	(meq/l)	(Cl^-/SO_4^{2-})	(eq/l resin)	(mg/l)	(mg/l)	(mg/l)	
769	770	1.00	0.267	20	396	264	6.37
1149	390	2.95	0.304	18	438	247	6.07
1538	390	3.95	0.319	15	417	244	6.21
1538	245	6.29	0.332	12	442	238	6.55

The choice of a suitable end point for controlling
the ion-exchange operation can improve the separation of
nitrate from sulphate, by which the adsorption of
sulphate should be displaced as much as possible in an
operation cycle. As shown in Table 12, the release of
sulphate and the operation capacities were obviously
increased as the end point (EP) of operation was changed
from 20 mg NO_3^-/l to 40 mg NO_3^-/l for the residual nitrate
in effluent. Meanwhile, there were little changes in the
average nitrate concentrations in effluent. Because
relatively larger amounts of sulphate were released into
the treated water near the end of the operation cycle,
choosing a relatively higher end point as controlling
limit for residual nitrate could reduce the steady-state
concentration of sulphate in spent regenerant.

Table 12
The inflence of the end point (EP) of operation on mass
balance (IMAC HP555)

Cycle	Capacity (eq/L resin)		Average NO_3^- in effluent (mg/l)		Average SO_4^{2-} in effluent (mg/l)	
	EP=20 ppm	EP=40 ppm	EP=20 ppm	EP=40 ppm	EP=20 ppm	EP=40 ppm
1	0.289	0.331	12	16	369	400
2	0.271	0.300	9	12	396	415
3	0.297	0.332	10	13	394	412
4	0.260	0.278	10	13	368	383
5	0.331	0.353	6	9	410	422
6	0.282	0.323	8	13	398	427
7	0.305	0.336	9	13	406	425
8	0.305	0.337	9	11	418	432
9	0.296	0.327	10	14	435	452

5

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Claims

    1. A process for removal and destruction of dissolved nitrate from water containing the same, which comprises

5 -   a removal step in the form of an anion-exchange operation, where nitrate is eliminated from said water in the form of a more concentrated solution thereof, said anion-exchange operation being nitrate selective;

10 -   a destruction step, where said more concentrated nitrate solution is subjected to an electrolysis operation for nitrate destruction by electrochemical reduction thereof;

  -     a conditioning step, where solution resulting from

15   the destruction step is adjusted by the addition of chloride ions so as to enable use of said solution as a regenerant in the anion-exchange operation while maintaining an operating capacity of said anion-exchange operation which is substantially

20   unchanged from one anion-exchange operation to another; and

  -     a recycling step, where solution resulting from the conditioning step is used as a regenerant in the anion-exchange operation.

25   2. A process according to claim 1, wherein the anion-exchange operation is selective to nitrate, sulphate and chloride in said specific decreasing order.

    3. A process according to any one of the preceding claims, wherein the electrolysis operation is performed

30 in a two-compartment electrochemical cell.

    4. A process according to claim 3, wherein the two-compartment electrochemical cell is equipped with cation-exchange membranes.

    5. A process according to any one of the preceding

35 claims, wherein, in the conditioning step, said solution resulting from the destruction step is adjusted by the addition of chloride ions so that the variability of the

operation capacity of said anion-exchange operation is less than 10 %.

6. A process according to any one of the preceding claims, wherein, in the conditioning step, said solution resulting from the destruction step is adjusted to a chloride concentration higher than about 5 %wt.

7. A process according to any one of the preceding claims, wherein, in the conditioning step, said solution resulting from the destruction step is adjusted to a ratio in equivalents of chloride to sulphate higher than about 6.

8. A process according to any one of the preceding claims, wherein, in the conditioning step, said solution resulting from the destruction step is adjusted by the addition of chloride ions corresponding to a regeneration level higher than about 350 g NaCl/l ion-exchange resin.

9. A process according to any one of the preceding claims, wherein all of the solution from the removal step is passed to the destruction step.

10. A process according to any one of the preceding claims, wherein all of the solution resulting from the destruction step is conditioned and passed to the recycling step.

11. A process according to any one of the preceding claims, which is performed continuously for a complete re-use of regenerant.
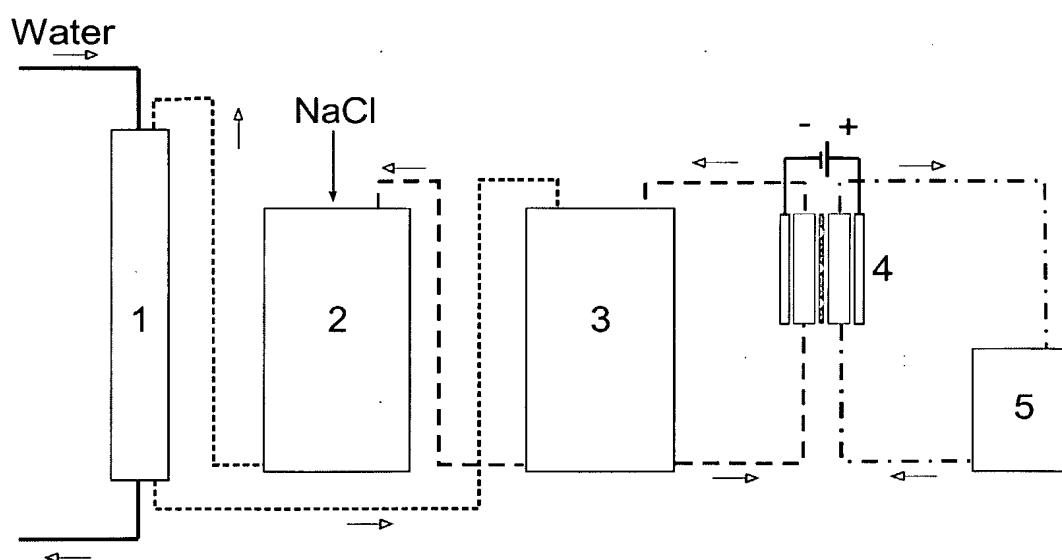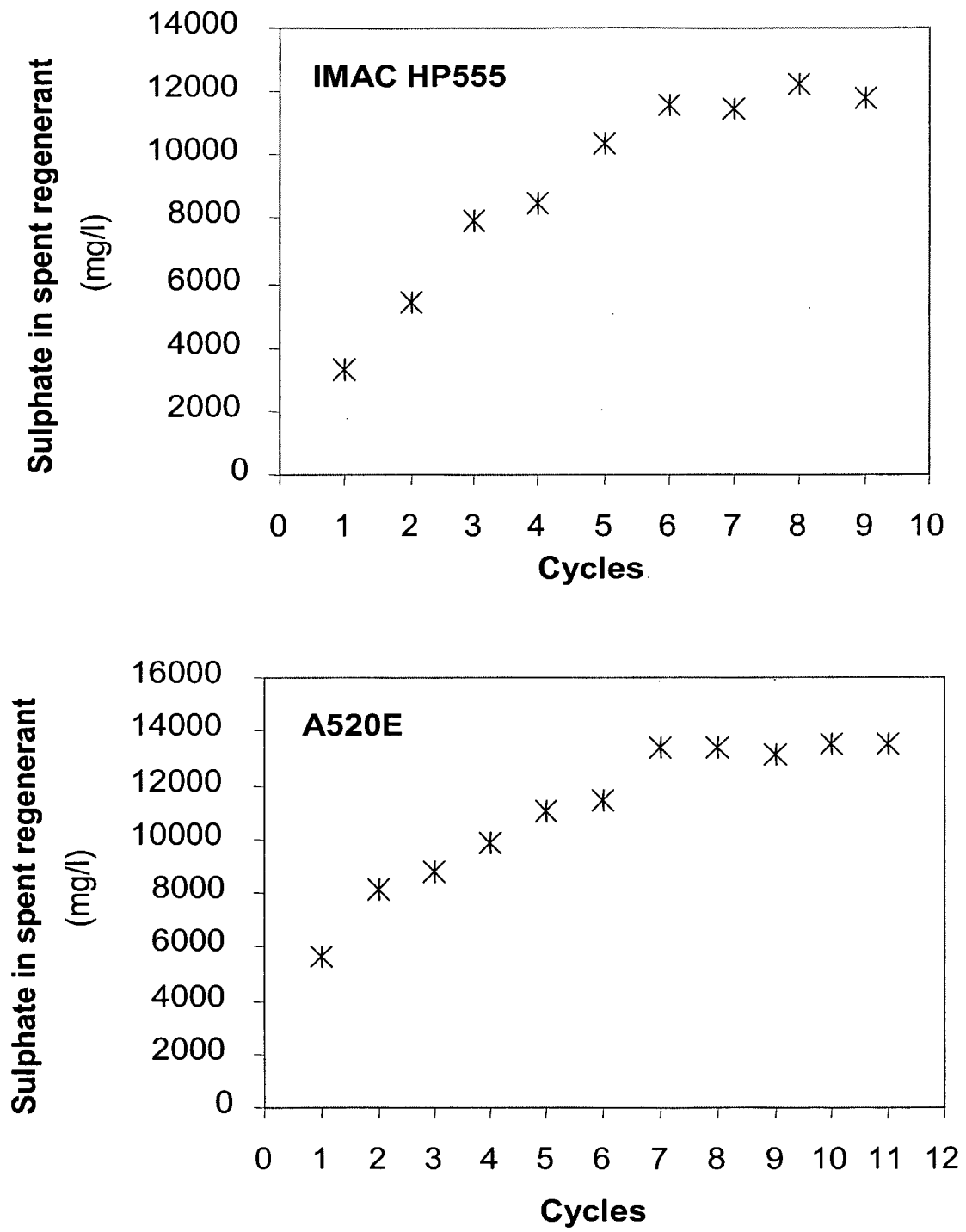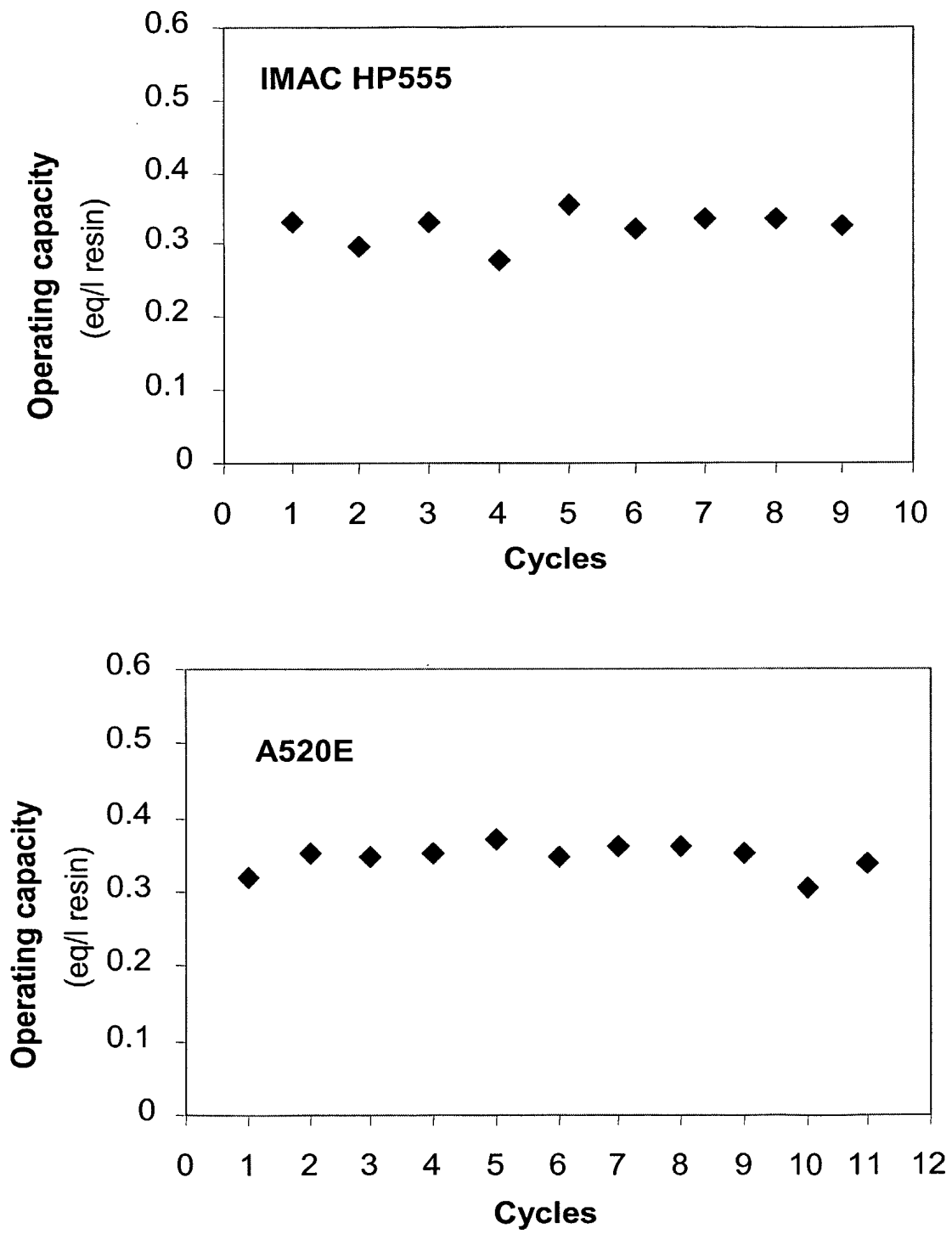
Figure 1

Figure 2

Figure 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 02/00360

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C02F 1/42, C02F 1/461, B01J 41/00, B01J 49/00 // (C02F 1/42, 101:16), (C02F 1/461, 101:16)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C02F, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 2002	1 4 -10- 2002
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Jens Waltin/ELY Telephone No. + 46 8 782 25 00

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C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0291330 A2 (ANGLIAN WATER AUTHORITY), 17 November 1988 (17.11.88), see the whole document -- --------	1-11

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